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ASSESSMENT OF SUPERCONDUCTIVITY ENHANCEMENT CLAIMED TO OCCUR IN SMALL PARTICLE-NORMAL METAL MATRIX COMPOSITE SUPERCONDUCTORS

by

M. Ashkin

February 20, 1978

Westinghouse Electric Corporation

Research and Development Center

Pittsburgh, Pennsylvania 15235

AFOSR Contract No. F49620-78-C-0031

Research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, United States Air Force

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ABSTRACT

The claims of substantially enhanced superconducting transition temperature, T_c, and upper critical field, H_{c2}, are judged implausible. This conclusion was reached by comparing the claims with what is theoretically expected using current theories, experimental results, and concepts of superconductivity of high-T_c material. However, the Battelle approach holds some promise of achieving both good mechanical and good superconducting properties in a practical conductor. AC losses and proximity effects in the composites need careful consideration in the evolution of a practical composite conductor.

1. INTRODUCTION

1.1 Preamble

An evaluation is presented of recent claims of substantially enhanced superconducting properties found in composites formed with high-T_c small particles dispersed in a metallic matrix. These composites are produced by the inventions described in U. S. Patent No. 4,050,147[1] and in related German patent disclosures.[2] A summary of this evaluation, dated January 25, 1978, was submitted earlier to AFOSR.[3]

1.2 Battelle Inventions

At Battelle-Frankfurt a whole host of inventions (patent disclosures) was generated by H. Winter, all apparently stimulated by the original Tsuei wire, a composite conductor containing Nb_3Sn discontinuous filaments in a Cu (bronze) matrix.[4] The latest disclosure and the corresponding U. S. patent cited in Section 1.1 described an arc-plasma process of generating A15 or B1 microparticles (aerosols) of 100 to 500 Å diameter, the coating of these particles with copper by arc plasma or other methods, compacting and extruding into tubes and wires.[1,2] Table 1 summarizes composite properties that were reported by Battelle. For comparison Table 2 gives the properties of high-T_c superconductors that are widely accepted. The enhancement of A15 T_c and H_{c2} values compared with those of Table 2 was such that, if true, it would amount to a revolutionary breakthrough in superconductivity. The impact upon technology would be enormous since most present problems and limitations would be effectively removed.

The Battelle material differs in at least two essential ways from the materials of other ductile small particle or discontinuous filament composite conductors.[4-6] The superconductor is initially produced

Table 1

Properties of Battelle's Composites

Reference		DOS 2,516,747 10-28-1976(2)	U. S. Patent, 4,050,147 9-27-1977(1)			
Superconductor	--	V_3Si	V_3Si	Nb_3Sn	Nb_3Sn	Nb_3Sn
Particle Size	Å	100	100	300	200	100
Matrix Material	--	Cu	Cu	Cu	Cu	Cu
Coating Thickness	Å	40	40	--	?	40
Fraction of Superconductor	vol %	20 to 30 (given) ∿ 17 (calculated)	∿ 17 (calculated)	35	20	∿ 17 (calculated)
Critical Temperature, T_c	K	29	29 (onset of transition)	21	23	24.7
Upper Critical Field, H_{c2}	T	100	100	47	57	71
At Temperature	K	?	4.2	?	?	?
Critical Current (Self ?), J_c	A m^{-2}	5×10^{11}*	no data	7×10^9	9×10^9	9×10^9
Tensile Strength	MN m^{-2}	no data	no data	740	780	820
Strain to Failure	%	7	no data	9	7	7

*No degradation upon straining.

as small particles (100 to 500 Å) which even without mechanical reduction are smaller in size than the filaments in other composites. It also was formed as a ultrapure stoichiometric compound while for the other ductile conductors the A15 was formed in situ by solid state diffusion of Sn through or out of a matrix into dispersed Nb particles. In the latter process, the conversion of Nb to Nb_3Sn may be incomplete and the Cu-Sn matrix may still contain Sn "impurities" limiting its conductivity. The outstanding superconducting properties are presumably based on the small particle size. A monotonic increase in T_c, H_{c2} and critical-current density, J_c, with decreasing particle size was claimed.

Table 2

Typical Properties of High T_c Superconductors

Group	Nominal Formula	T_c K	H_{c2} (4.2 K) tesla	Filamentary J_c (12 T, 4.2 K) 10^9 A m^{-2}
A15	V_3Ga	14	∿ 20	5 to 10
	V_3Si	∿ 17	∿ 20	
	Nb_3Sn	17 to 18	19 to 20	1 to 2
	Nb_3Al	18 to 19	∿ 30	
	Nb_3 (Al_3Ge)	∿ 20	∿ 40	
	Nb_3Ga	∿ 20	∿ 30	
	Nb_3Ge	∿ 22	30 to 40	
B1	NbN	15 to 16	13 to 32	
	Nb (C,N)	17 to 18	10 to 20	

1.3 Scope of Evaluation

It is certainly true that some superconducting properties are different for a material in bulk form and in small particle form. It is well established that the magnetic behavior in the superconducting state

is different for the two sample forms.[7] The size of the critical current without dispute depends on grain size (see Figure 1).[8,9] Most researchers accept that large changes in the superconducting transition temperature T_c occur when some bulk materials with low T_c's are prepared in small particle form.[10] Apart from Winter's claims, no results are reported of any increase of T_c brought about by fabricating a high-T_c compound in small particle form.

Since it is difficult to theoretically predict T_c in most materials, it is not possible to dismiss or accept the Winter results in a clean, clear-cut way. What has been done is to critically review the claims using established thinking on high-T_c materials. The claims will be compared with what is theoretically expected using current theories, experimental results, and notions of superconductivity of the A15's and B1's.

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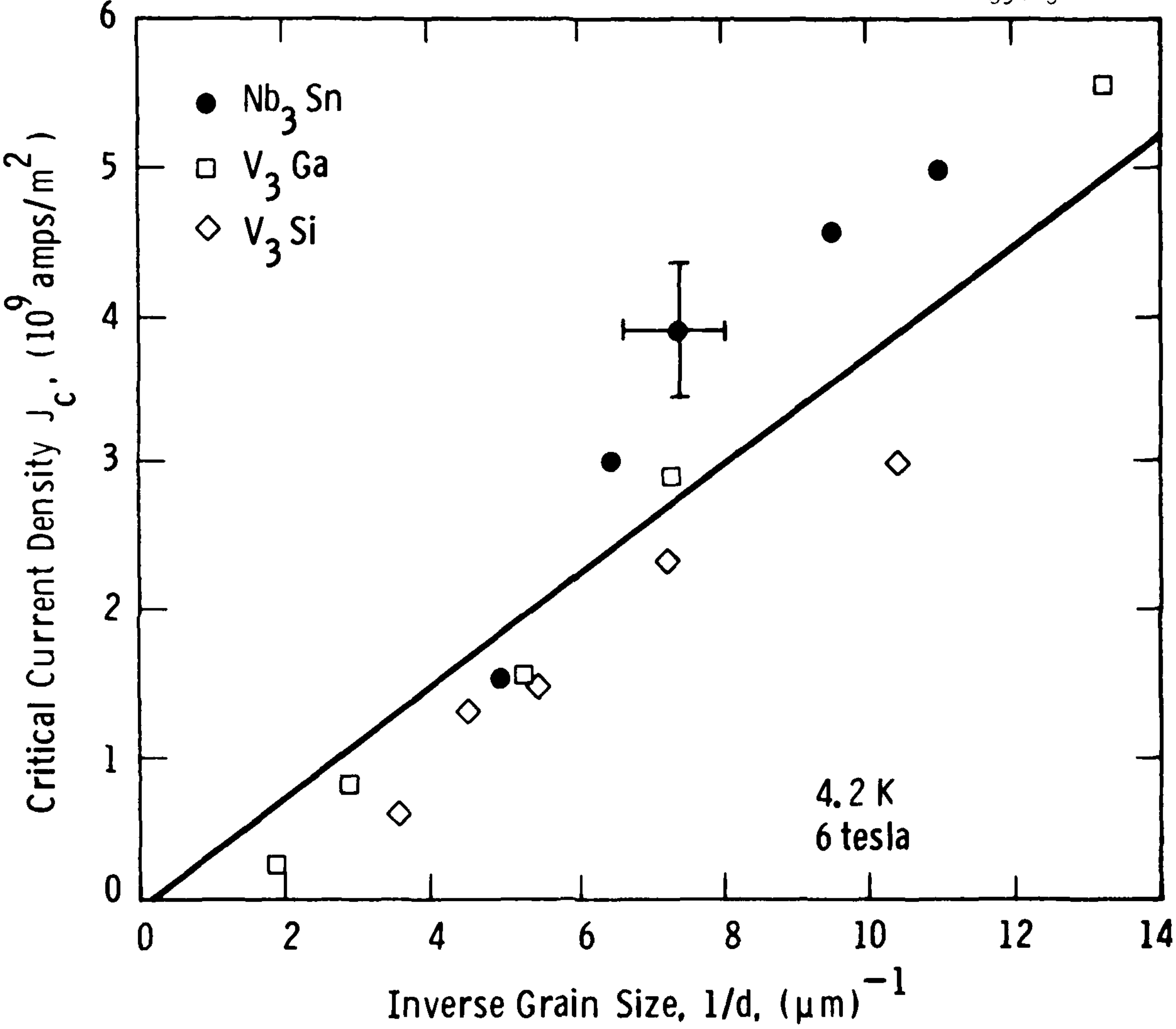

Fig. 1 — Critical current density vs inverse grain size for diffusion-processed, filamentary wires of Nb_3Sn, V_3Ga and V_3Si; after Livingston.[9]

2. T_c-ENHANCEMENTS

2.1 General

The BCS[11] explanation of superconductivity is based on an attractive interaction between two electrons. In contrast in a non-superconducting state electrons repel each other rather than attract each other. The attraction results from one electron polarizing the lattice near the second electron. This is called the "phonon mediated" or "plain phonon" mechanism. The detailed interpretation of a large number of experiments[12] leads one to accept this phonon mechanism and no other. Many other sources of attraction[13] are proposed but all lack experimental verification and can be safely ignored for this appraisal.

Many T_c-enhancement theories or proposals abound even within the conventional phonon framework; of these only the lattice softening mechanism (a decrease in the average vibrational frequency) is experimentally supported.[10] This appears to be the mechanism that motivated H. Winter. A theoretical basis for believing that lattice softening leads to high-T_c superconductivity was provided by McMillan.[14] The uncritical use of McMillan's formula does indeed predict large T_c's on softening. However, more careful evaluation shows that "softening" can result in either a positive or a negative change in T_c.

The sensitivity of T_c to lattice softening was carefuuly studied by Bergmann and Rainer.[15] Though they did not study the A15's or nitrides, one can use their work to assess the possibility of T_c enhancement in general and specifically for interesting high-T_c materials.

2.2 McMillan Formulation

Current discussions about high-T_c materials are in terms of λ, η, $\alpha^2 F(\omega)$ which can best be introduced through the McMillian interpolation formula for T_c[14]

$$T_c = \frac{<\omega>}{1.2} \exp\left[-\frac{1.04\ (1+\lambda)}{\lambda - \mu^*\ (1 + 0.62\lambda)}\right] \quad (1)$$

where $\mu^* \sim 0.1$ to 0.2. The electron-phonon coupling parameter λ is

$$\lambda = 2 \int_0^\infty \alpha^2 F(\omega)\ d\omega/\omega \quad (2)$$

The $\alpha^2\ F(\omega)$ is the spectral function of the attractive interaction and depends on microscopic material details. Under favorable conditions $\alpha^2\ F(\omega)$ can be obtained from tunneling experiments though it is not available in sufficient detail for most high-T_c A15. Results for fine, clean particles also do not exist. In some cases $\alpha^2 F(\omega)$ is derived from a phonon density of states using an $\alpha^2 F(\omega)$ which is assumed or calculated. This latter density of states which is obtained from neutron diffraction experiments is available for an increasing number of materials including many of the A15's, and B1's. Theoretical calculations of $\alpha^2 F(\omega)$ are still unreliable for T_c predictions. The remaining quantity in McMillan's formula is the moment

$$<\omega> = \frac{\int \alpha^2 F(\omega)\ d\omega}{\int \alpha^2 F(\omega)\ d\omega/\omega} \quad (3)$$

McMillan showed that λ can be written as (M is some weighted ion mass)

$$\lambda = \frac{N(0)\ <I^2>}{M\ <\omega^2>} = \frac{\eta}{M\ <\omega^2>} \quad (4)$$

where η is a pure electronic property and

$$\langle\omega^2\rangle = \frac{\int d\omega\,\omega\,\alpha^2F}{\int d\omega\,\alpha^2F/\omega} \tag{5}$$

which is mainly vibrational.

2.3 Lattice Softening T_c- Enhancement Mechanism

The lattice softening-T_c enhancement theme is: while keeping η constant decrease $\langle\omega^2\rangle$ and thereby increase λ and T_c. Lattice softening can be accomplished by producing small particles in which the atoms on the particle surface are bound by a smaller number of chemical bounds to the interior atoms which results in decreased force constants. When a large fraction of the atoms in a samples are on or near the surface as in very small particles the average vibrational frequency is lowered by an amount sufficient to shift the weight $\alpha^2F(\omega)$ to lower frequencies. The parameter λ, Eq. (2) is very sensitive to low frequencies. A T_c enhancement interpreted as from lattice softening was observed in isolated, clean Al and In fine particles of $\sim$ 100 Å diameter.[16] In the same work, no change in T_c was observed in Pb. Table 3 contains the enhancement factors T_c/T_c(bulk) for a group of elements.[10]

The first observation drawn from Table 3 is that amorphous superconductors show the largest T_c-enhancements when there are enhancements. However, experiments show that the highest T_c in an A15 compound is obtained for an ordered, stoichiometric material.[17] In most Nb-based compounds, a measure of this state, besides the high-T_c, is a minimum lattice parameter (see Figure 2). An exception is that Nb-rich A15 Nb-Sn may have a small lattice parameter than the stoichiometric compound. These experiments include annealing[18-20] and radiation damage studies.[21] Because of this strong correlation between order and high-T_c for the A15's, T_c-enhancement through softening by forming amorphous materials is not viable for these materials. This leaves softening through surface effects in small particles as the only reasonable T_c-enhancement mechanism.

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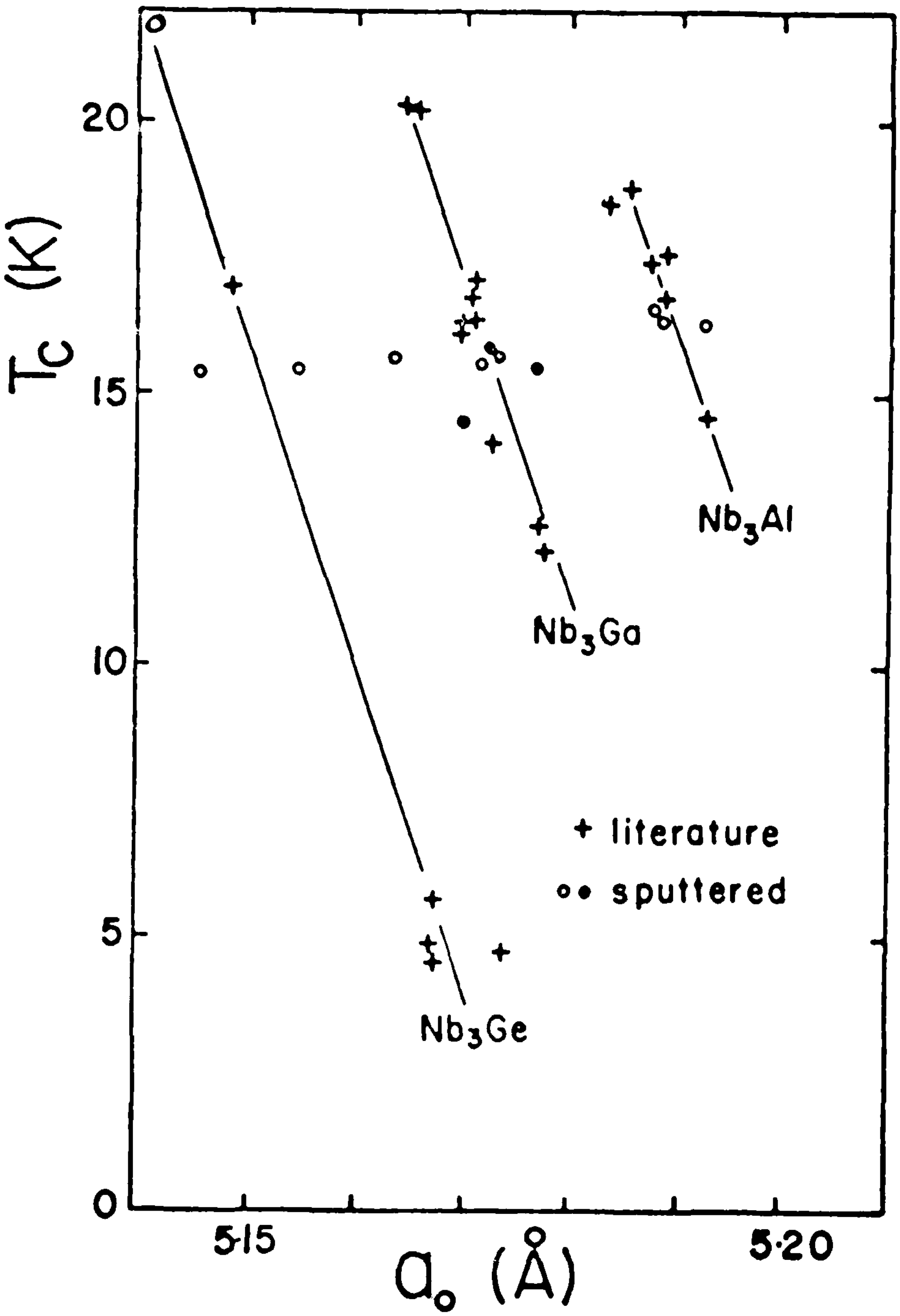

Fig. 2 — Superconducting transition temperature, T_c, vs lattice parameter a_0 for the A15 compounds Nb_3Ge; Nb_3Ga and Nb_3Al; after Johnson and Douglass, ref 44

Table 3

Measured T_c-enhancement factors. The superscript b denotes values in bulk. From Reference 10.

	λ	T_c^b	IP	TF	O_2	LTD	LTD,TF	LTD,C
Al	0.38	1.16	1.6	1.8	1.9	2.30	4.8	5.0
Zn	0.38	0.85				1.60	2.1	
Sn	0.60	3.72		1.1	1.1	1.30	1.6	1.9
In	0.69	3.40	1.1	1.1	1.1	1.20	1.3	1.4
Tl	0.71	2.38				1.10		
Hg	1.00	4.16		1.0		0.95		
Pb	1.12	7.19	1.0	1.0	1.0	1.00	1.0	

Legend: IP, isolated particles, TF, thin films. O_2, evaporation in oxygen. LTD, low-temperature deposition, LTD, TF, low-temperature deposition, very thin films. LTD, C, low-temperature co-deposition with organic molecules, oxides, semiconductors, semimetals, or metals.

To study the plausibility of this mechanism we list some properties of the A15 and B1 materials in Table 4.

Table 4

Materials properties and parameters used in T -enhancement calculations. a_o is the bulk lattice constant and the superscript b denotes that the items are bulk quantities.

	a_o Å	T_c^b K	λ^b	μ^{*b}
V_3Si	4.722 4.722	17.00 17.00	1.28 1.10	0.16 0.20
Nb_3Sn	5.289	18.00	1.30	0.20
NbN	4.390	14.94	0.82	0.10
$NbN_{0.73}C_{0.17}$	4.420	17.60	0.92	0.10

The λ listed are derived from McMillan's formula and depend on the choices of μ^* and Debye temperature.[22] Superconducting tunneling data provide a consistent set of μ^*, λ and $\langle\omega\rangle$.[25] Tunneling data are not available for many d- and f-band materials for the practical reason that they are difficult to prepare pure and their short coherence length makes results sensitive to surface impurities.[23] The materials listed are the ones that Winter has claimed to have unusually enhanced mechanical and superconducting properties.

2.4 Enhancement Model Based on McMillian Formula

All materials listed in Table 4 have a $\lambda \gtrsim 0.8$. For the materials listed in Table 3, the measured T_c-enhancements decrease with increasing λ and are nonexistent for the large λ. A simple model used by Matsuo et al.[24] for their T_c-enhancement experiments on Sn, Al and Pb small particles (see Table 3) is now applied to Winter's materials and particle sizes. The results of this model for Sn, Al, and Pb are consistent with the decrease in T_c-enhancement with increasing λ.

The details of the derivation of the enhancement factor can be found in Ref. 24 and is based on McMillan's formula [Equation (1)] and expressions for $\langle\omega\rangle$ and $\langle\omega^2\rangle$ from Dickey and Paskin.[25] These moments for small particles are decreased or softened because of the decrease in force constants coming from a decrease in the number of nearest-neighbors of atoms near the surface. Results for different size particles are shown in Figure 3.

An important assumption in all the softening-enhancement models and in the simple model we use is that in the expression $\lambda = \eta/M\langle\omega^2\rangle$ η is taken as nearly or completely unchanged when the lattice expands. This assumption was an extension of McMillian's observation that η is nearly constant within a given class of materials. The parameter μ^* is also assumed unchanged in this model. Putting aside for now the validity of this assumption on η for the materials in Table 4, the whole change in λ is from a change in $\langle\omega^2\rangle$ and the change in T_c is from changes in $\langle\omega^2\rangle$ and $\langle\omega\rangle$.

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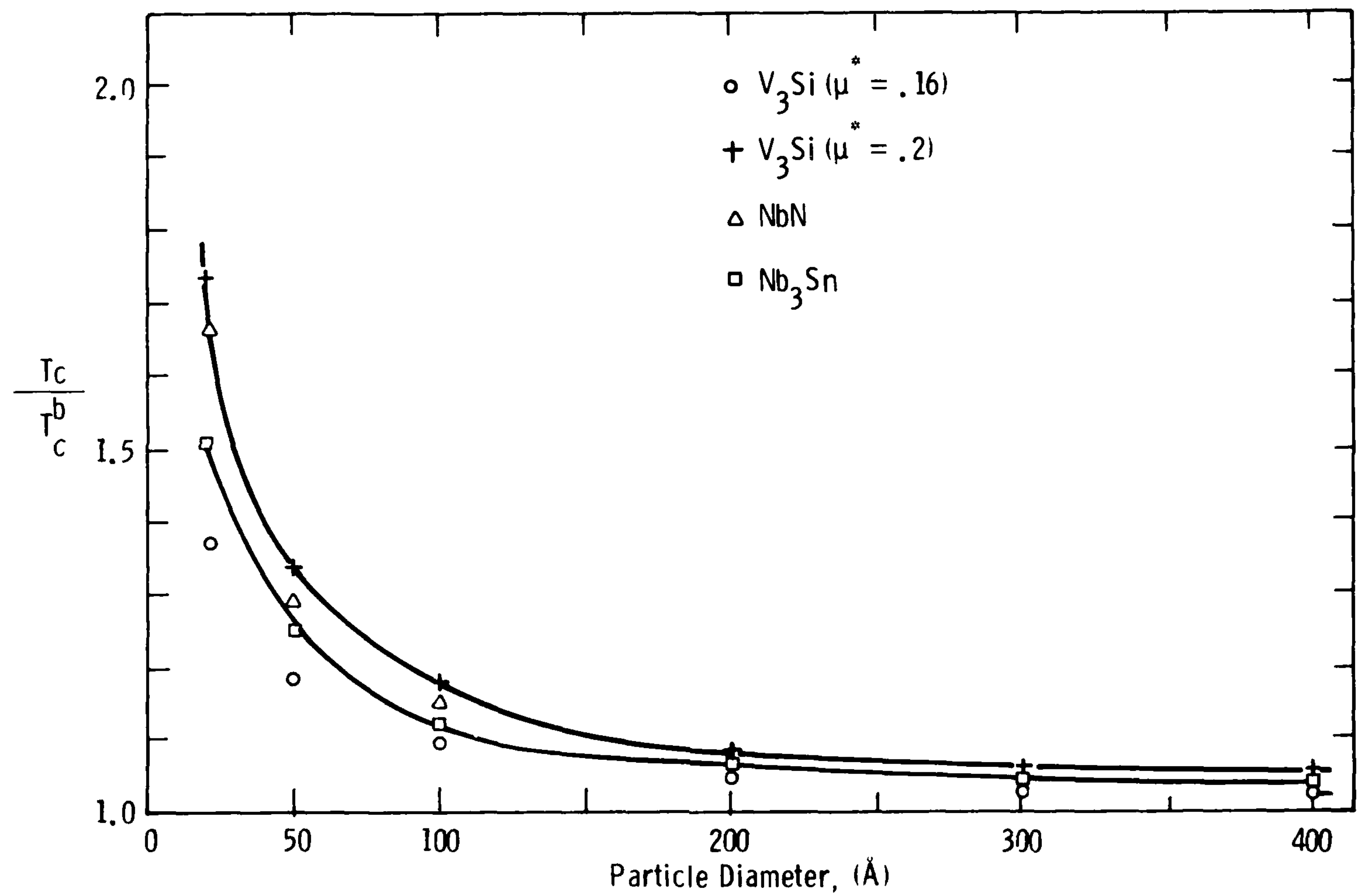

Fig. 3—T_c- enhancement factor T_c/T_c^b vs particle diameter (Å) calculated by the theory of Matsuo et al, ref 24

Table 5 compares the T_c of Winter and Sethna[5,6] and the T_c derived theoretically from Matsuo et al.[23] Winter's Nb_3Sn values are to quote Reference 6, "the resulting" or "showed the" superconducting property listed. The V_3Si "showed superconducting fluctuations already at 29 K." In all cases these data far exceed the theoretical prediction. One could speculate on the divergence, but without an independent check on the experimental results one tends to distrust the claims. There is also a complete lack of discussion by Battelle on little things like experimental details of T_c measurements. One is aware that in a well equipped and expertly staffed low-temperature laboratory these measurements are routine, however startling results (even proprietary ones) require for their belief a detail exposition.

2.5 η and T_c-Enhancement

The theory used to generate T_c/T_c^b in Figure 3 and Table 5 does not incorporate any difference in η between the bulk and a small particle. A small particle of a material should have a lower density (larger lattice constant, large molar volume) than the same substance in bulk because of the lattice relaxation (expansion) accompanying softening. This may have a large deleterious effect on T_c.

Hopfield[26,27] observed that in the A15 Nb_3Sn the Nb atoms are closer together than in the element Nb and suggested this as the origin of the large increase of η for Nb_3Sn over those of Nb. A rough dependence of $\eta \sim (\text{molar volume})^{-3.5}$ seems to hold for the A15's and for V and Nb. The decrease in η in small particles because of relaxation if large enough could overcompensate for a decrease in $\langle\omega^2\rangle$ because of softening with a resulting overall decreased λ (and T_c). The situation in the A15's with respect to the assignment of dominance for high-T_c to soft modes or electronics (η) is admittedly far from simple or clear.[23]

Table 5

Comparison of Winter's Data from Table 4 with Theoretical Results. Calculations for B1 Compounds are also Included.

Material	Winter's Data [1,2]				From Matsuo et al. [24] Calculated				Superconducting Parameters [22]	
	T_c^b K	d^b Å	T_c K	d Å	T_c^b K	$\frac{T_c}{T_c^b}$	T_c K	d_o Å	λ^b	μ^*
V_3Si			~ 29.0	100	17.00	1.10 1.18	18.70 20.10	100 100	1.28 1.10	0.16 0.20
Nb_3Sn	17.8	2×10^4	21.0	300	18.00	1.05	18.90	300	1.30	0.20
Nb_3Sn			23.0	200		1.07	19.26	200	1.30	0.20
Nb_3Sn			24.7	100		1.13	20.34	100	1.30	0.20
NbN					14.94	1.15	17.18	100	0.82	0.10
$NbN_{0.73}C_{0.17}$					17.60	1.12	19.71	100	0.92	0.10

Legend: T_c^b = T_c of bulk material.

d = particle diameter.

d^b = particle (grain) size in bulk.

λ^b = λ of bulk material

μ^* = Coulomb pseudopotential.

2.6 Low Frequency Phonon Effects on T_c

The analysis in Appendix A, crude as it is, indicates that softening that may exist in Winter's A15 materials will change T_c negligibly. The nitride and carbide composites will behave similarly.[30]

2.7 Proximity Effects[31]

These effects can only lower the T_c of composites like Battelle's The usual configuration for experimental and theoretical studies of these effects is a sandwich of two metals evaporated one onto the other. One metal is superconducting in bulk (S), the other is normal or only weakly superconducting (N). The T_c of the sandwich is lower than that of the higher-T_c superconductor alone, the decrease depending on the thicknesses, D_N and D_S, of the two films (see Figures 8 and 9).[32,33]

The Battelle material is a composite with isolated superconducting particles dispersed uniformly in a normal metal matrix. Roughly 20% by volume is superconductor in the best material. To estimate the decrease in T_c, this configuration is replaced by a sandwich with thicknesses D_S and D_N, $\xi_N \approx \xi_S(T_{cs})$ and $D_N/\xi_N \gtrsim 4$ (see Ref. 34). Figure 10 plots the calculated reduced temperature T_c/T_{cs} vs $d_s = D_S/\xi_S(T_{cs})$, where T_c is the composite transition temperature and $T_{cs} = T_c^b$ the isolated superconductor transition temperature. For the situation where ~ 1/3 by volume is superconductor $d_s \sim 2$ and $T_c/T_{cs} \sim 0.5$. A more accurate calculation that used measured resistivities and specific heats, allowed for the normal metal thickness and proper geometry[46] should show the same large depression.

For the proximity effect to operate good electrical contact between N and S must exist and N must not diffuse into S.

Extensive work at Westinghouse[35] under an AFOSR contract and elsewhere on Cu- (Sn-Ge)- Nb systems showed that there is little diffusion of Cu into the A15 compounds. The good electrical contact between the A15 and the coating Cu is assured by the cleanliness of the process.

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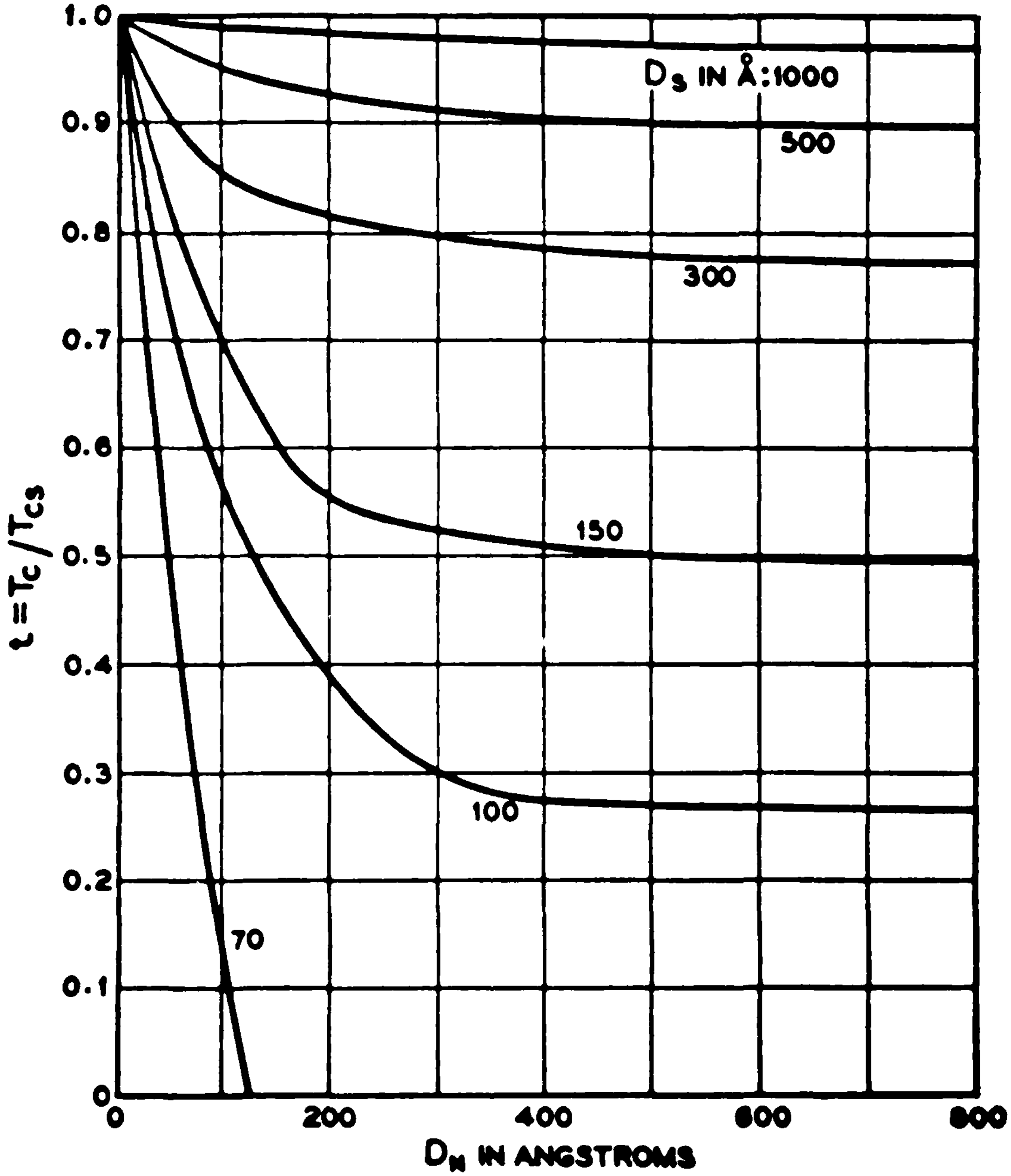


Fig. 8—Typical experimental curves of reduce transition temperature t of Pb-Cu sandwich vs Cu film thickness D_n for a range D_s of Pb film thickness; from Werthamer, ref 34

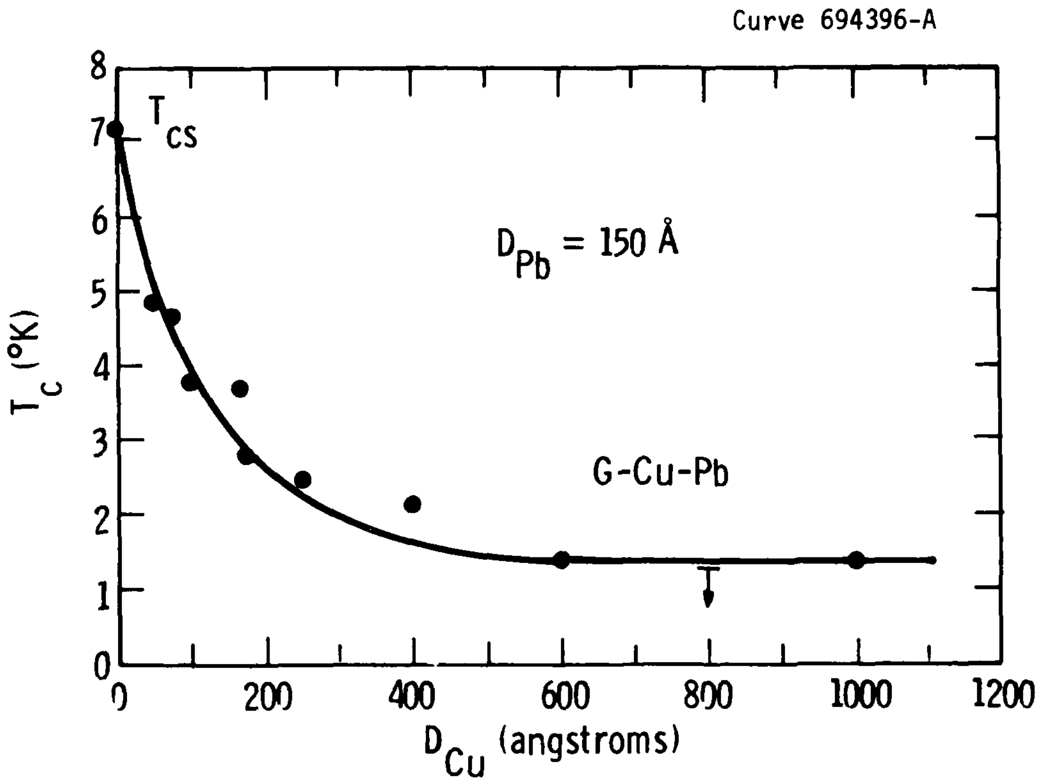


Fig. 9—Transition temperature of Pb-Cu sandwiches for a constant lead film thickness of 150 Å; from Hauser, ref 33

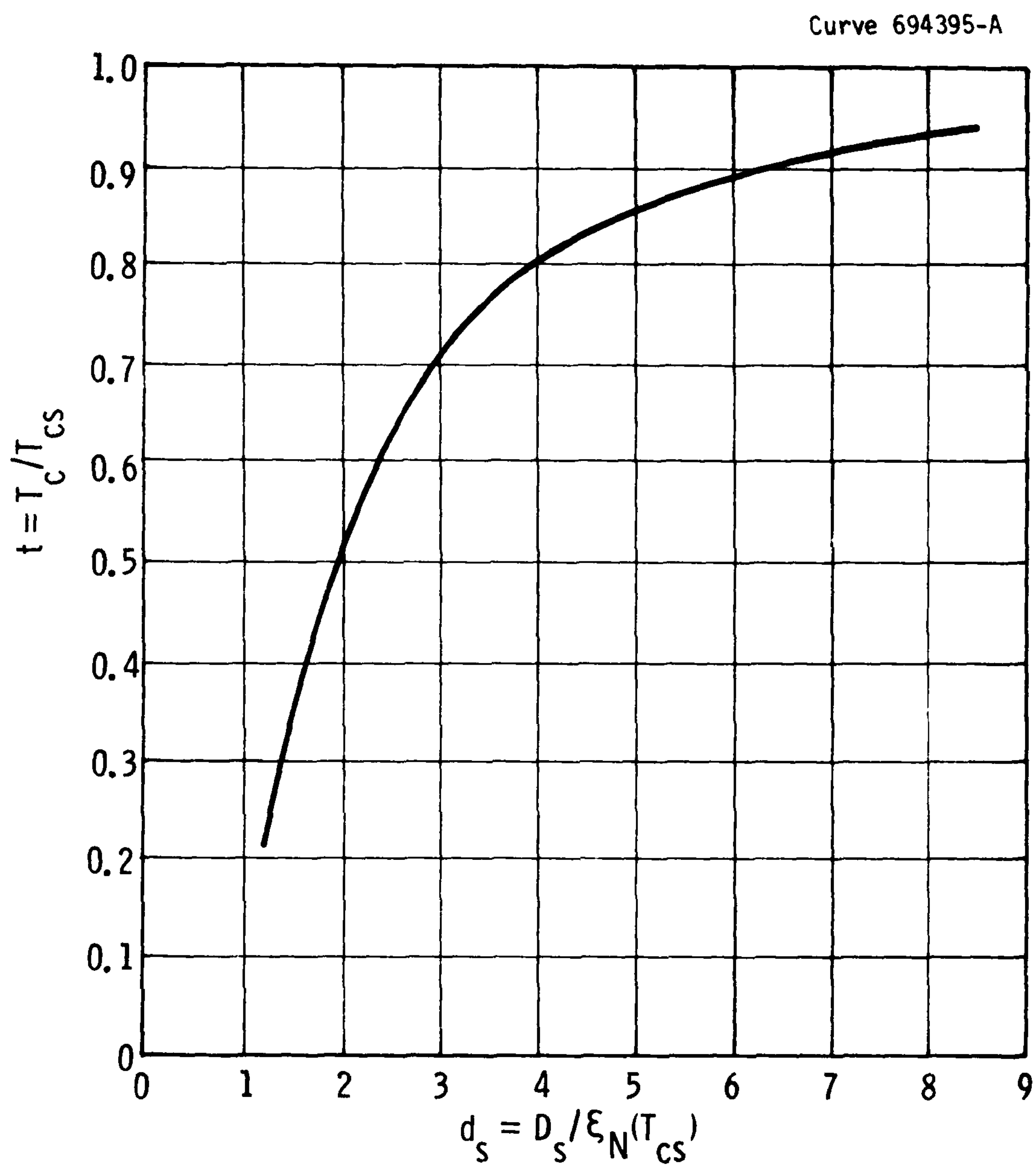


Fig. 10—t vs d_s calculated for a superconductor-normal metal sandwich with $\xi_N = \xi_s$ and "thick" normal layer. T_c and T_{cs} are transition temperatures of sandwich and isolated bulk superconductor, respectively; D_s is the superconductor film thickness and ξ_N is normal metal coherence length at $T = T_{cs}$

Investigations of the extent of the proximity effect and usefulness of obvious ways to defeat it are useful areas to pursue.

If the proximity effect is operating in the Battelle composite and the probability is high that it is, the inescapable conclusion of this section is that the Battelle process produces sizeable T_c-depression $\gtrsim 1/2$ rather than a T_c-enhancement.

2.8 Further Considerations

There are two other considerations bearing on T_c-enhancements. When λ becomes too large materials can become unstable and transform electronically or structurally.[36,37] The transformed state may have a lower T_c or not even be superconducting. The situation is far from clear. The second consideration is the role of a sharply varying density of states at the Fermi surface in raising T_c. This consideration was first studied by Labbé, Barisic and Friedel,[38] and recently by Nettel and Thomas.[39] For present purposes an important point is that T_c depends on an average of the density of states about the Fermi energy; the range of energies in the averaging is roughly the width of phonon spectrum. Small particle effects could change this averaging by moving the Fermi surface relative to the density of states structure and changing the density of states. The consequences of these changes for T_c-enhancement, needless to say, are difficult to predict.

3. UPPER CRITICAL FIELD H_{c2}

Large enough magnetic fields can destroy the superconductivity of a material. This upper limit depends on temperature, T, and sample condition and is called the upper critical field H_{c2} (T). For extremely thin or small samples the limiting field may depend strongly on the sample dimensions showing an increase with decreasing dimensions. If surface superconductivity is not considered, for the high-T_c materials this sensitivity to dimensions is only important for sizes < < 50 Å.

The Werthamer et al. theory[40] (WHH) relates the H_{c2} at T = 0 K to the normal state resistivity ρ, electronic specific heat γ and T_c. This relation is

$$H_{c2}\ (0) = f\ (\alpha,\ \lambda_{so})\ \rho\ \gamma\ T_c$$

where the known function (see Hake Ref. 41) f (α, λ_{so}) accounts for paramagnetic and spin orbit effects. The parameters α, λ_{so} also depend on the material properties. The variation of γ with size probably can be neglected for this assessment. The T_c-enhancements of Winter are insufficient alone to account for the large H_{c2}-enhancements of their materials. This requires the manipulation of resistivity by small particle and composite effects to achieve the large reported H_{c2}-enhancements.

As stated in the U. S. Patent No. 4,050,147[1] the H_{c2}-enhancement was motivated by Watson's work on granular superconductors: lead particles in an insulating matrix. In such a granular superconductor, the conductivity is limited by intergrain tunneling which can lead to a very large resistivity.

For most high-T_c materials the zero temperature Ginzburg-Landau coherence length < 75 Å and for particle sizes greater than this coherence

length, the resistivity of the particle not the composite enters the WHH theory. Furthermore the metallic matrix of the Battelle composites do not provide tunneling barriers to limit the conductivity. If anything the composite normal state resistivity will be <u>lower</u> than that of the superconductor.

In bulk Nb_3Sn, H_{c2} (0) = 22 tesla, T_c = 17.8 K and a mean free path $\ell \sim 13$ Å is achieved ($\rho \propto 1/\ell$). From the reported H_{c2} data (Table 1), mean free paths in the superconducting particles were extracted using the conventional Werthamer et al. theory. Winter's best results in 100 Å Nb_3Sn particles are H_{c2} = 71 tesla, T_c = 24.7 K with a mean free path $\ell \simeq 5$ Å. It is only remotely possible that extra scattering which would shorten the mean free path is coming from the superconductor-normal metal boundary. Thus, this mean free path is felt to be unphysical when compared with the interatomic spacing [1/2 (lattice constant) = 2.64 Å] and, in view of the strong correlation between T_c, order and stoichiometry, incompatible with the high-T_c.

Because of the short coherence length for Nb_3Sn it does not seem possible to increase H_{c2} through small particle effects. The resistivity would be limited by intragrain scattering not particle size. Experiments also support this view for Nb_3Ge(42) and it is reasonable to extend this view to all A15 and high-T_c materials. The situation for the B1's, especially NbN, is not clear cut. Some experiments on the H_{c2} of NbN show no size effects(42) and support a view similar to the one that obtains for the A15. Other experiments show a strong dependence of H_{c2} on film thickness.(45) Conclusion about H_{c2}-enhancements in the B1's cannot be made with the present information.

4. CONCLUSIONS AND DISCUSSION

Theoretical and experimental work point to the conclusion that no T_c-enhancements from small particle effects should be expected for high-T_c materials. Similarly, no H_{c2} enhancements are expected from particle sizes in the 100 Å range. The claims of Winter are believed to be unreasonable extrapolations from an incomplete theoretical basis.

To reinforce our evaluation we report that negotiations to obtain samples from Battelle for an independent evaluation by Westinghouse resulted recently in admission by Battelle that these data were "not directly measured . . . but rather derived by extrapolation from measurements applying theoretical methods." Our present conclusion is that a breakthrough in obtaining higher T_c and H_{c2} did not and is not expected to occur in fine particle composites.

Though not documented in this report, an evaluation of the mechanical properties was made. In contrast to the negative assessment of the superconducting behavior of the Battelle composites, the mechanical properties and the mechanical load tolerance claimed are plausibly superior to both, conventional filamentary and "in-situ" wire. Whether microparticle superconducting composites can be fabricated by Winter's approach or some other technique to exhibit advantageous mechanical properties together with reasonable T_c's, H_{c2}'s and J_c's, typical of A15 and B1 bulk superconductors, remains to be seen.

Work in this direction was performed at Westinghouse employing a technique different from the arc plasma method. With partial support of AFOSR, Charles et al. at Westinghouse R&D Center have recently produced fine particles of Nb by liquid sodium reduction, the particle size ranging between 100 and 800 Å. Critical temperature measurements of loose particle agglomerates of Nb gave $T_c \approx 8$ K while bulk Nb has

T_c 9.3 K. We consider this to be an encouraging result in view of unavoidable contamination with sodium oxygen, etc. It suggests that, perhaps, fine powders of A15 or B1 compounds would also be obtained with T_c's approaching bulk values. Would the T_c not be degraded too much after molding into the normal matrix a ductile superconductor could result exhibiting an attractive trade-off between superconducting and mechanical properties. An abstract of a talk on this work was submitted to the "March" meeting of the American Physical Society (March 1978).[43]

In considering the arc-plasma synthesis it is important to note that due to extremely fast quenching rates, and the ability to incorporate controlled amounts of impurities, the process might be capable of producing quantities of metastable (Nb_3Ge, Nb_3Si?) or new compounds not obtainable by metallurgical methods. Westinghouse has a major arc-plasma process development for the Jet Propulsion Laboratory that is aimed at generating inexpensive pure silicon. A much smaller A15 or B1 arc-plasma synthesis program could "piggy back" on the on-going effort.

To utilize the mechanical advantages of small particle composites while maintaining acceptable superconducting behavior, proximity effects must be defeated and ac losses limited. A good understanding of these effects is a first step in their control. The proximity effects can also be present even when conductions occurs by percolation as in recent "in-situ" configurations.

APPENDIX A

The analysis of Bergman and Rainer[15] identifies the important position of the phonon spectrum for T_c and provides insight into softening effects. Then work is briefly sketched and applied to the A15 in this appendix.

These authors use the functional derivative $\delta T_c/\delta\alpha^2F(\omega)$ to determine what frequency range of $\alpha^2F(\omega)$ is important for T_c. This derivative gives the change ΔT_c for a change $\Delta\left(\alpha^2F(\omega)\right)$ and is defined by

$$\Delta T_c = \int_0^\infty d\omega \frac{\delta T_c}{\delta\alpha^2F(\omega)} \Delta\left(\alpha^2F(\omega)\right).$$

Their calculations show that $\delta T_c/\delta\alpha^2F(\omega)$ rises linearly from zero to $\omega = 0$ and has a maximum at a frequency (energy) slightly above an "optimum" $\hbar\omega = 2\pi kT_c$ and then falls off (see Figure 4). No calculations are available or will be made of the functional derivative for the A15's. Instead the general properties or shape just described will be assumed to hold for this new group of materials.

The general form of this function is superimposed on $\alpha^2F(\omega)$ in Figure 5. The peak of $\delta T_c/\delta\alpha^2F$ is placed at $\hbar\omega = 2\pi kT_c$. Figure 6 shows a shift in $G(\omega)$ (density of state from neutron scattering) induced by a real softening; Nb_3Sn softens when the temperature is reduced from 297 K to 5.6 K. The change in $\langle\omega^2\rangle$ is $\sim$ 14%. If $\alpha^2F(\omega)$ in Figure 5 behaves in a similar way when softening is caused by small particle effects then a negligible change in T_c from softening would be predicted. The phonon density of states for V_3Si and V_3Ga are presented in Figure 7 along with the expected positions of the peak of $\delta T_c/\delta\alpha^2F(\omega)$ at $\hbar\omega \simeq 2\pi kT_c$ for the two high-temperature A15's. A comparison of $G(\omega)$ and $\alpha^2F(\omega)$ in Figure 5

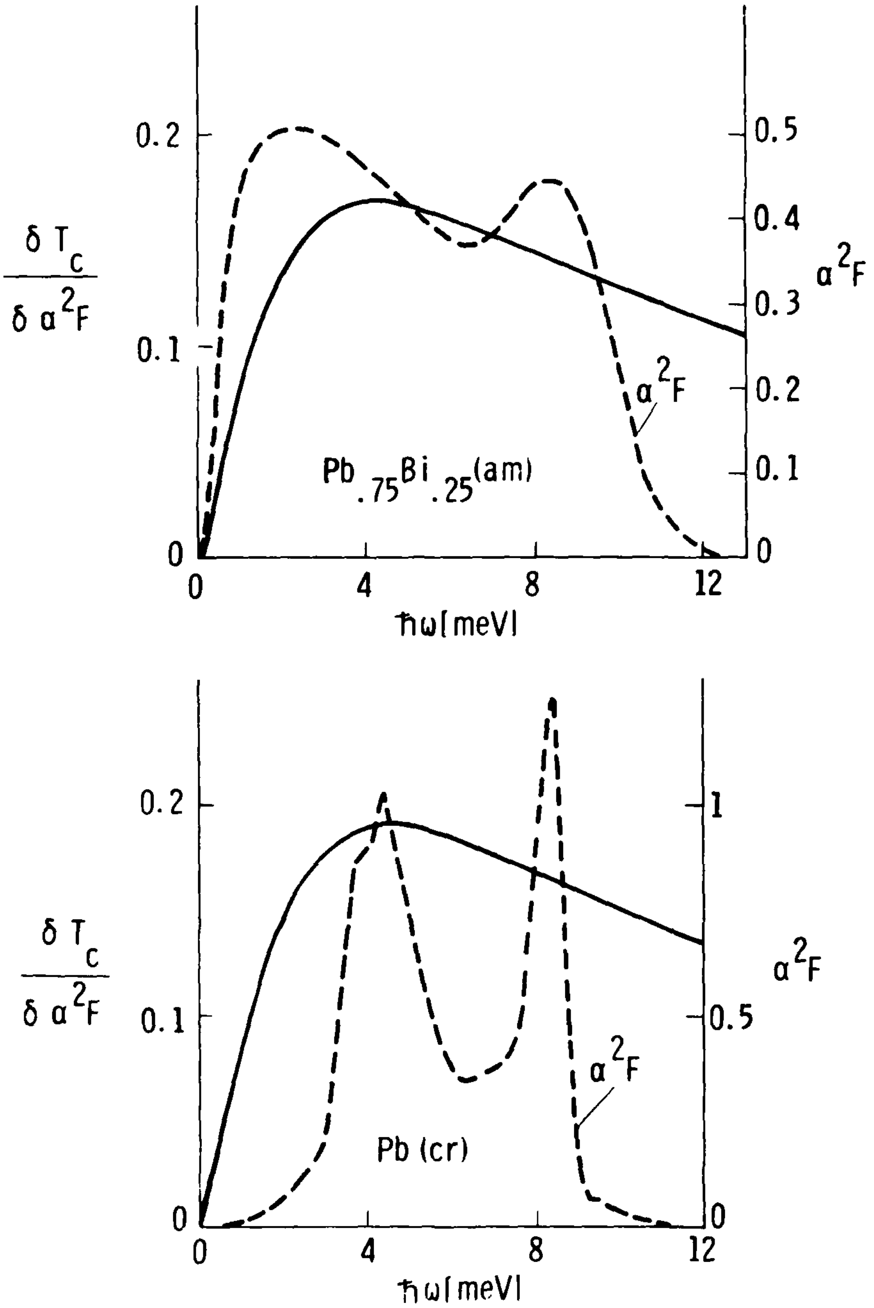
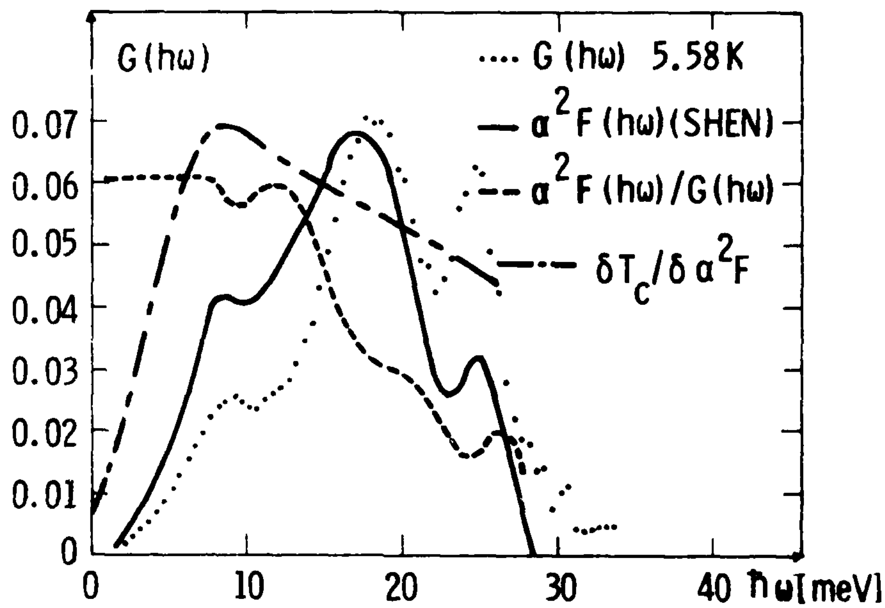
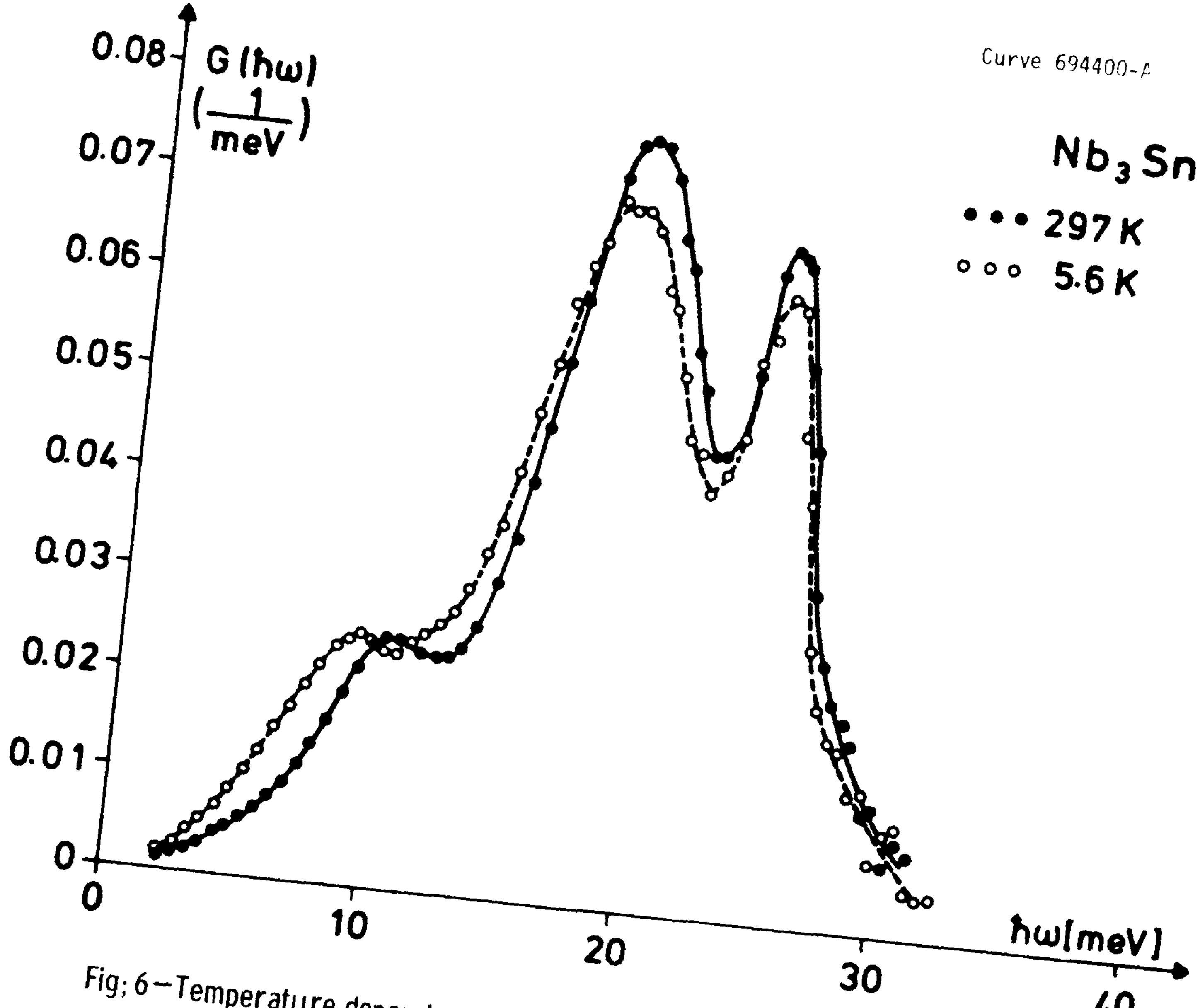


Fig. 4—The functional derivative $\delta T_c/\delta \alpha^2 F(\omega)$ and the spectral function $\alpha^2 F(\omega)$ vs energy $\hbar\omega$ for crystalline (cr) and amorphous (am) Pb; from Bergmann and Rainer, ref 15

Curve 693700-A



Fig; 5—Schematic $\delta T_c/\delta \alpha^2 F(\omega)$ vs energy $\hbar\omega$ superposed on a plot of $\alpha^2 F(\omega)$ vs $\hbar\omega$ for Nb_3Sn; after Schweiss et al, ref 28



Fig; 6—Temperature dependence of phonon density of states G (ħω) for Nb_3Sn; from Schweiss et al, ref 28

Curve 694398-A

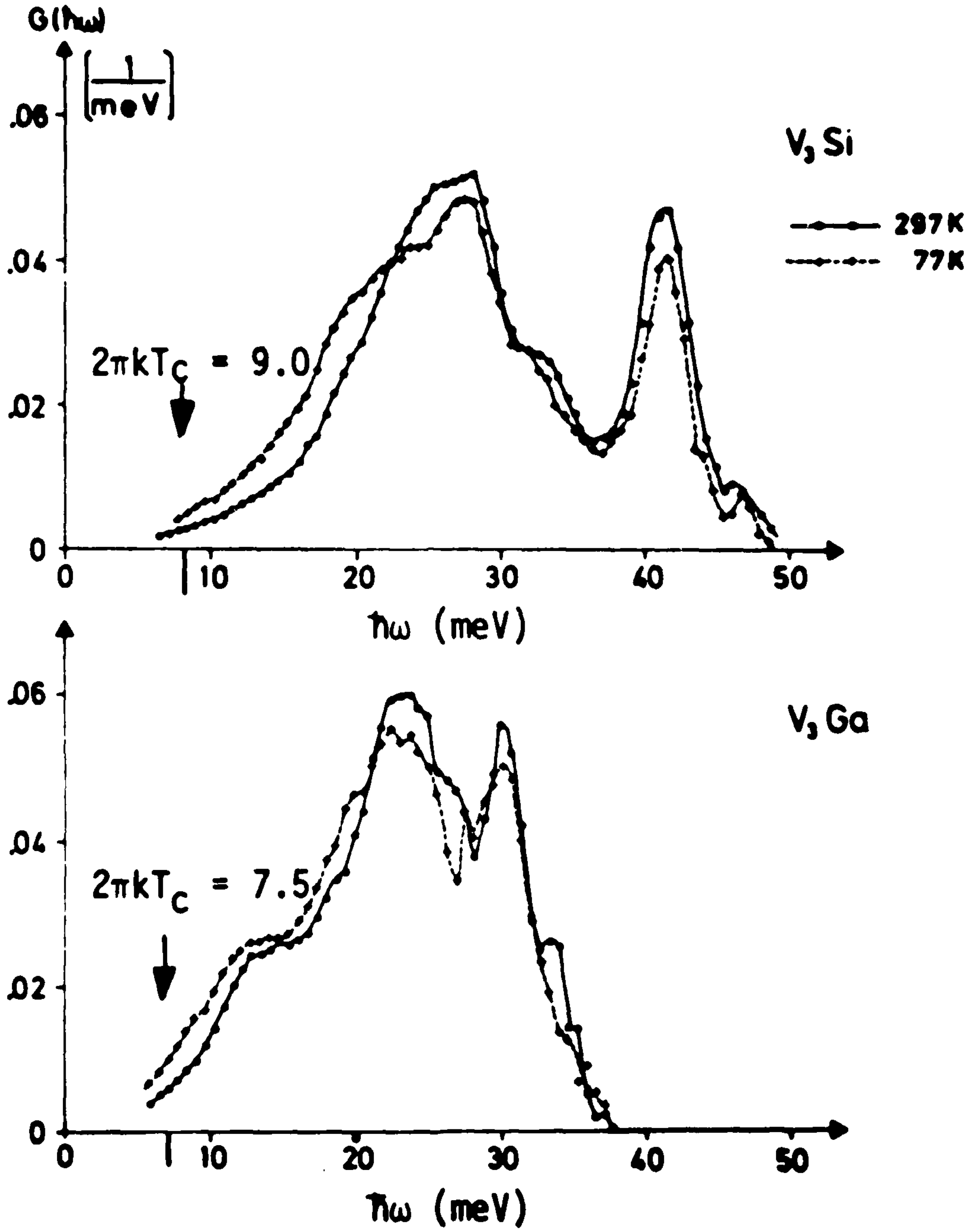


Fig. 7—Temperature dependence of phonon density of states G (ω) vs energy ħω for V_3Si and V_3Ga. The position of the peak of $\delta T_c/\delta \alpha^2F(\omega)$ is marked by the arrow; G(ω) after Schweiss et al ref 28

for Nb_3Sn shows their similarity for low frequencies. We assume the same holds for the other A15's and because of the smallness of $G(\omega)$ near $\hbar\omega \approx 2\pi kT_c$ negligible changes in T_c from softening is expected. This is consistent with experiments that transforming and nontransforming V_3Si have T_c's differing for at most several tenths K.[29] Presumably the two forms have softened differently. Two other A15's, V_3Ge and Nb_3Al look like V_3Si at low frequencies and therefore by analogously reasoning would not show significant changes in T_c on softening. The change in [illegible] on cooling V_3Si is [illegible] 18%.[28]

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